Macromolecular Rapid Communications
www.mrc-journal.de

Segmental Mobility Studies of Poly(*N*-isopropyl acrylamide) Interactions with Gold Nanoparticles and Its Use as a Thermally Driven Trapping System

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Thermal desolvation of poly(*N*-isopropylacrylamide) (PNIPAM) in the presence of a low concentration of gold nanoparticles incorporates the nanoparticles resulting in suspended aggregates. By covalently incorporating <1% acenaphthylene into the polymerization feed this copolymer is enabled to be used as a model to study the segmental mobility of the PNIPAM backbone in response to gold nanoparticles both below and above the desolvation temperature, showing that there is a physical conformational rearrangement of the soluble polymer at ultralow nanoparticle loadings, indicating low affinity interactions with the nanoparticles. Thermal desolvation is capable of extracting >99.9% of the nanoparticles from their solutions and hence demonstrates that poly(*N*-isopropylacrylamide) can act as an excellent scrubbing system to remove metallic nanomaterial pollutants from solution.

1. Introduction

With the increasing use of inorganic nanomaterials in commercial and industrial products,[1] there a need to improve our understanding of polymer–particle interactions at the molecular level.[2–4] Most of the recent studies in this field have studied polymer micelles (or other aggregate structures),[5] or focused on the assembly[6]/delivery[7] of inorganic particles post-polymer modification, often with little emphasis being placed on the changing solution properties of single polymer chains. Recent developments in our ability to interrogate polymer-conformational responses to stimuli have allowed us to carry out experimental trials on polymer/gold nanoparticle interactions at low concentrations; to investigate the physical response of the temperature responsive, azo-initiated poly(*N*-isopropyl acrylamide) to gold nanoparticles and provide evidence of the decreased polymer segmental mobility on the initial polymer/nanoparticle interactions.

Importantly, due to the stimuli responsive nature of the polymers used, this binding is highly efficient at extracting these materials from solution via thermal desolvation. Following several decades of international research into the synthesis and applications of nanotechnology, concerns have arisen over the effects that these nanoparticle metals may have on the environment,[8,9] particularly to aquatic biomes.[10] A range of wastewater remediation techniques which can extract or immobilize metal nanoparticles from solution have been proposed. One of the most promising leads is the use of supramolecular hydrogelators to remove a range of metal pollutants,[11,12] including nanoparticles,[13,14] from aqueous solutions, over timescales of up to 48 hours.

A potentially faster method of immobilizing metal ions would be to use a macromolecular "switch," such as a stimuli responsive polymer, to sequester nanoparticles out of solution. Poly(*N*-isopropylacrylamide) (PNIPAM) is a polymer that undergoes a lower-critical solution temperature (LCST) transition at 33 °C, and is one of the most extensively studied examples of a stimuli responsive material.[15–17] A range of low-molecular weight brush PNIPAM coated nanoparticles have previously been investigated and the polymer-coating was observed to retain its responsive properties, changing in volume as the nanoparticles were driven across the polymer's LCST.[18] However free polymer chains can still interact with nanoparticles in a similar manner to that of supramolecular hydrogels, and their stimuli driven response could be used as an instantaneous trigger to immobilize nanoparticles.

Covalently labelling polymers with fluorescence labels is a proven method for modelling the solution behavior, and therefore conformational responses to stimuli, of solvated polymer chains. Poly(NIPAM-*co*-ACE) has previously been used to contrast the different solution properties (via alterations in segmental mobility) of the polymer in water and methanol[19] or in the presence of a range of salts.[20] In this study the same label is used to both measure directly the conformational collapse of the stimuli-responsive polymer with temperature and to infer the conformational rearrangement indicating chain end interactions between the label and the gold nanoparticles. The thermal properties of the polymer are then demonstrated to be

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/marc.201800090.

DOI: 10.1002/marc.201800090

an excellent tool by which these inorganic nanomaterials may be removed from solution. To the best of our knowledge this is the first time segmental mobility study of this type to have been carried out on low concentration polymer/gold nanoparticle mixtures.

2. Results and Discussion

2.1. Experimental Details

Synthetic and instrumental details, including the synthesis of P(NIPAM-*co*-ACE) and the Au nanoparticles, are contained within the Supporting Information. PNIPAM polymers with fluorescence tags with a unimodal size distribution (M_n = 76 kDa, $Đ$ = 1.84) containing <0.1% ACE fluorescence copolymer tag were prepared. Measurements of this tag, including time correlated excited state lifetime studies, were carried subsequently undertaken. The fluorescence decay profiles were fitted using a single exponential equation

$$I(t) = I_0 \exp\left(-\frac{t}{\tau_f}\right) \quad (1)$$

where I_0 is the intensity at time zero (upon excitation) and the lifetime being referred to here is the fluorescence excited state decay of the dye (τ_f). These measurements can determine both the dye excited state lifetime and its rotational diffusion, contingent on the use of polarizing filters during the experimental setup.[20] Polarized anisotropy (r) measurements were therefore fitted using the modified equation

$$r(t) = r_\infty + (r_0 - r_\infty)\exp\left(-\frac{t}{\tau_c}\right) \quad (2)$$

where r_∞ is the sample anisotropy at an infinite time, r_0 its initial anisotropy, and τ_c is the determined rotational correlation time. Gold nanoparticles of unimodal size distribution were prepared and characterized by dynamic light scattering (DLS), UV–vis absorbance, and transmission electron microscopy (TEM), all of which confirmed an average reproducible particle diameter across multiple batches to be 20 nm (S.D. 2 nm).[21,22]

2.2. Thermal Desolvation of Polymer/Nanoparticle Solutions

Thermal desolvation of the labelled PNIPAM in dilute solution leads to the aggregation of multiple polymer chains and eventual phase separation of the mixture. Particle sizing of the collapsed PNIPAM globules has shown that in dilute solutions a stable suspension containing moieties with a diameter of 120 nm is formed, consistent with previous studies.[23] When this heated globule is exposed to gold nanoparticles there is a slight increase in the observed particle diameter, however the size increases greatly when the polymer collapse is triggered in the presence of an equivalent nanoparticle concentration. The desolvating PNIPAM appears to incorporate the nanoparticles into the aggregates as they form, following the coil-to-globule transition, and form a particle of greater diameter (**Figure 1**).

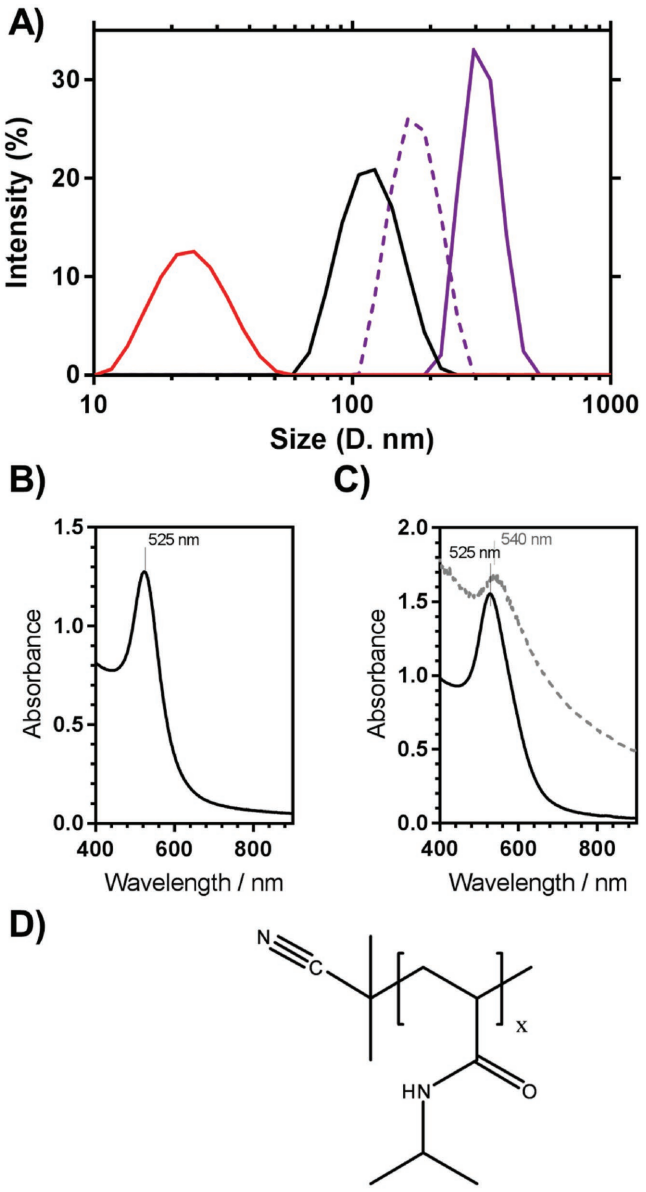

Figure 1. A) DLS particle size distribution of Au nanoparticles (—), desolvated PNIPAM suspensions (—), predesolvated PNIPAM suspension exposed to nanoparticles (—), and PNIPAM/nanoparticles mixtures desolvated (...). B) UV–vis absorbance profiles of Au nanoparticles. C) UV–vis absorbance profiles of Au nanoparticles/PNIPAM mixtures at 20 °C (black, complete)/45 °C (gray, dashed). D) Structure of azo-initiated PNIPAM polymer.

Desolvation of PNIPAM and its subsequent deposition around the nanoparticles appears to lead to the nanoparticles being incorporated into the aggregate, as evidenced by a slight shifting and broadening of the nanoparticles UV–vis absorbance peak, a situation that was not observed to occur when the same formulation was mixed at an elevated temperature (45 °C). Energy-dispersive X-ray spectroscopy (EDX) analysis of dried samples confirmed the incorporation of significant amounts of gold within the polymer aggregates.

An additional experiment was carried out in which nanoparticles were added to both swollen and collapsed polymer

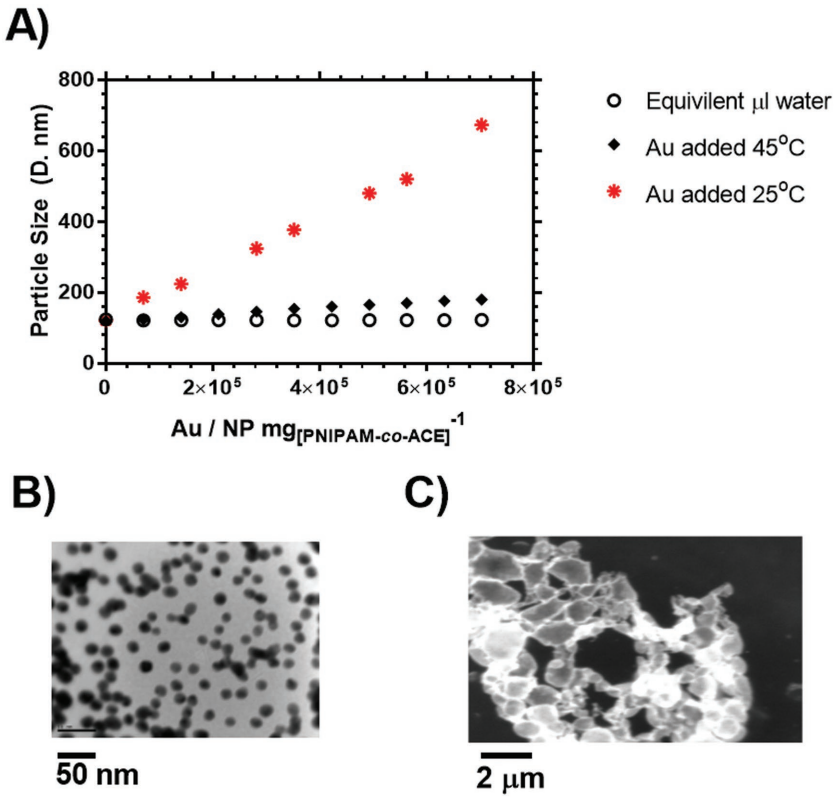

Figure 2. A) DLS Particle Size of collapsed polymer globule (T = 45 °C) with addition of Au nanoparticles per mg of PNIPAM in solution. Nanoparticles added to preheated collapsed polymer at 45 °C, nanoparticles added at 25 °C then heated to desolvate the globule and the comparative size of polymer diluted with addition of equivalent concentration of pure water. B) TEM image of gold nanoparticles. C) SEM image of thermally desolvated PNIPAM/Au nanoparticle aggregates.

solutions and the particle size measured at 45 °C (**Figure 2**). When the nanoparticles were added to preheated polymer solutions the size of the collapsed polymer aggregates increased with increasing nanoparticle concentration. Globules generated from an equivalent polymer/Au NP ratio, that was formed by heating following the addition of nanoparticles, exhibited a far greater increase in size than those heated prior to Au NP addition. Comparing the significant difference in size between the two systems it is reasonable to conclude that nanoparticles cannot easily penetrate nor leave the globule after it has collapsed, demonstrating the ability of the collapsing polymer to trap nanoparticles, isolating them from the solution.

2.3. Fluorescence Measurements

The covalently incorporated ACE fluorescence label was used to measure the conformation of PNIPAM during its collapse. The monomer label exhibits no change in its excitation/emission wavelengths but does exhibit different fluorescence properties when copolymerized due to being shielded from the solvent by the macromolecule (**Figure 3**a). Fluorescence quenching studies were carried out at 25 °C in order to study the interaction between the gold nanoparticles and the PNIPAM shielded ACE label (Figure 3b–e). Quenching tests were also carried out on the dye monomer (acenaphthylene (ACE)) in methanol, this solvent being deemed the most appropriate solvent as the monomer ACE is not soluble in water. The Stern–Volmer plot is based on the following equation

$$\frac{I_f^0}{I_f} = 1 + K_{SV}\left[Q\right] = 1 + K_q\tau_0\left[Q\right] \quad (3)$$

where I is the intensity of the fluorescence, K_{SV} is the apparent gradient of the Stern–Volmer plot (which is composed of two parameters: K_q is the quencher rate coefficient and τ_0 is the lifetime of the emissive state in the absence of quenching), and $[Q]$ is the concentration of quencher. This equation can also be used for comparing fluorescence lifetimes, where $K_{SV\tau}$ represents the quenching coefficient with respect to the excited state lifetime.

$$\frac{\tau_f^0}{\tau_f} = 1 + K_{SV\tau}\left[Q\right] \quad (4)$$

In this equation τ_c can be substituted with τ_f to facilitate correlation time Stern–Volmer studies.

Interestingly for P(NIPAM-*co*-ACE) no quenching of the fluorescence emission was observed upon the addition of nanoparticles up to 1×10^{12} particles per mg PNIPAM (Figure 3b), and that in the same ratio the fluorescence lifetime of the ACE label decreases from 32.3 to 30.5 ns (Figure 3d), after which point the fluorescence lifetime stabilized and did not decrease further with increasing gold nanoparticle addition. At higher gold nanoparticle concentrations the intensity decreased in line with the Stern–Volmer plot (K_q = 62 000 µL^{-1} S^{-1} for the region $[Q] > 1 \times 10^{12}$ Au NP per mg PNIPAM) (Figure 3b). Comparatively the ACE monomer is quenched by the gold nanoparticles at an apparently high K_{SV} but due to the lifetime of the ACE monomer being distinct from that of the polymerized P(NIPAM-*co*-ACE) the K_q was found to be comparable at 66 000 µL^{-1} S^{-1} (Figure 3c). This suggests that for $[Q] > 1 \times 10^{12}$ Au NP per equivalent mass of dye molecule the mechanism of quenching of the ACE is equivalent for both polymer and monomer systems.

Within the region $[Q] < 1 \times 10^{12}$ Au NP per mg PNIPAM there was no decrease in fluorescence intensity but a decrease in both the fluorescence lifetime (with $K_{SV\tau}$ calculated as 0.0008 µL^{-1}) (Figure 3d) and polarized correlation time (Figure 3e). This decrease is only seen for this region, and is indicative of a response of the polymer size to the presence of low concentrations of nanoparticles.

The ACE label is sensitive to the conformational status of the polymer and can be used to contrast the swollen/collapsed conformation it adopts below and above its LCST.[19] This is particularly evident in the anisotropy measurements which are not sensitive to fluorescence intensity or lifetime but respond

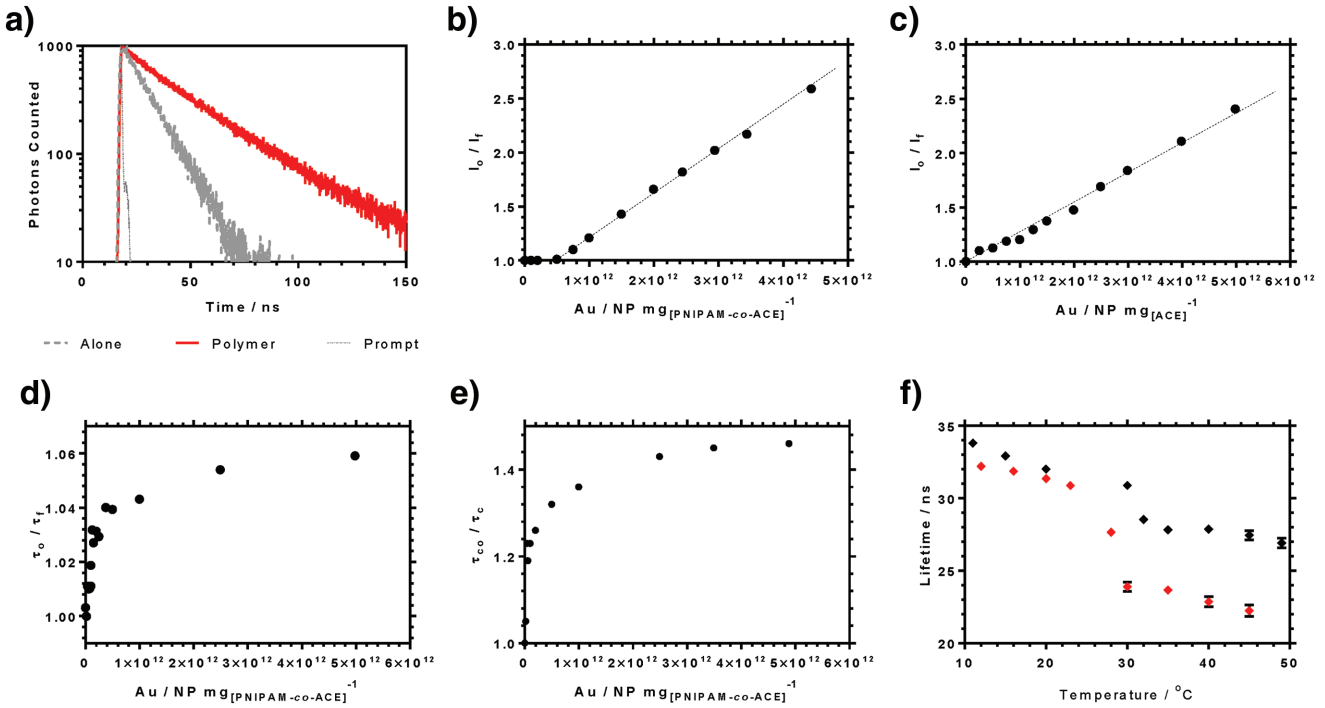

Figure 3. a) Fluorescence decay of monomeric ACE in methanol, copolymerized P(NIPAM-*co*-ACE) in water and silica prompt scattering light pulse. Experiments carried out at 25 °C. b–d) Stern–Volmer plots of gold quenching for b) fluorescence emission of P(NIPAM-*co*-ACE) following excitation at 290 nm, $K_{SV} = 0.002$ ([Q] > 100), c) fluorescence emission of ACE in methanol following excitation at 290 nm, $K_{SV} = 0.0014$ d) fluorescence lifetime of P(NIPAM-*co*-ACE) with gold added, $K_{SV\tau} = 0.0008$. e) Correlation time from time resolved anisotropy measurement with increasing Au concentration. f) τ_f of P(AA-*co*-ACE) alone (◆) and with 1000 µL gold (◇) in solution.

to the movement of the polymer in space during the lifetime of the measurement. At these low volume Au loadings (under 100 µL Au solution per mg polymer) depletion interactions maintains a degree of separation between the polymer shielded ACE label and the gold nanoparticles, thus polymer conformational rearrangement dominates the dye fluorescence properties.

The decrease in fluorescence lifetime at room temperature occurs with a polymer in an extended conformation. This was verified by heating a solution of mixed P(NIPAM-*co*-ACE) and Au nanoparticles from 10 to 50 °C and measuring the lifetime of the ACE label in order to contrast the collapse of the polymer with temperature (Figure 3f). In solution the polymer lifetime alone decreases by 5 ns as it desolvates at 30–32 °C. Addition of the nanoparticles decreases the lifetime of the polymer-ACE fluorescence decay by a few nanoseconds below the LCST but a marked decrease was observed at higher temperatures as the desolvating polymer incorporated the gold nanoparticles into the aggregates as they formed following the coil-to-globule transition of the macromolecule. Förster resonance energy transfer calculations indicate that the maximum average label—nanoparticle surface separation within the globule is ≈3 nm.

2.4. Thermal Nanoparticle Trapping System

As the data indicates that the stimuli-driven thermal desolvation of PNIPAM into aggregate particles incorporates nanoparticles from solution further tests were carried out to investigate the efficacy of removal of Au nanoparticles from solution. While at concentrations of 1 mg mL^{-1} PNIPAM desolvation occurs on the timescale of milliseconds the aggregate particles are stable in solution for several hours. This allowed their separation to be effected via low-speed centrifugation of the heated gold-polymer solutions (50 °C, 500 rpm, 1 min) to separate out the polymer from the supernatant. Using this method the desolvated polymer could be easily separated from the supernatant, which was tested for the presence of gold nanoparticles. Multiple repeat studies showed a 99.9% removal of the nanoparticles from the supernatant, while the polymer globule could rapidly be redissolved in cooler water to create a solution with an almost complete recovery of nanoparticles. These initial tests clearly demonstrate that polymer desolvation is an extremely rapid and efficient way of extracting nanoparticles from solution.

3. Conclusions

The polymeric response to the addition of low concentrations of gold nanoparticles has been studied, and it has been demonstrated that the thermally driven desolvation and aggregation of polymers is capable of not just incorporating nanoparticles, but is also an extremely efficient method for extracting nanoparticles from solution. Fluorescence tagging of the polymer backbone has allowed the polymer interactions with nanoparticles in both the solvated (coil) and desolvated (globular) states to be successfully studied. Both the fluorescence lifetime and segmental mobility (via polarized anisotropy measurements)

indicate that at extremely low nanoparticle concentrations there is a conformational rearrangement of the polymer. This indicates a potential chain end affinity of the nitrile group to the nanomaterial surface.[24]

This initial study demonstrates the efficacy of combining light scattering and fluorescence tagging techniques to study polymer/nanoparticle interactions and it is our hope that these systems can be further investigated, assisting future developments in materials science.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors would like to thank Stuart Fox for his assistance in preparing SEM, TEM, and EDX images for this manuscript. S.G.H. would like to thank the Science Foundation Ireland's ETS Walton Visitor awarded scheme grant (11/W.I/12085). R.H., who kindly donated his time to assist with instrument analysis and sample preparation for this work, is an MRC funded Research Associate (MR/N501888/2).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

gold nanoparticles, segmental mobility, temperature responsive polymers, time correlated fluorescence

Received: January 31, 2018
Revised: March 19, 2018
Published online: May 2, 2018

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